

Synthesis and Characterization of pH-Sensitive Networks Containing Degradable Poly(1,3-dioxolane) Segments

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ABSTRACT: pH-sensitive networks were obtained by radical copolymerization of telechelic poly(1,3-dioxolane) (PDXLDA) with acrylic acid (AA). PDXLDA was synthesized by acrylation of the corresponding dihydroxylated polyacetal (polyDXL) with AA in pyridine. The copolymer networks of poly(AA-*b*-DXL) showed pH sensitivity due to —COOH groups, which are insoluble in any solvents, but can swell in water or good solvents. The swelling behavior is closely related to the solvents and is composition-dependent. The networks containing polyDXL segments can be decrosslinked under acidic conditions due to the low ceiling temperature of polyDXL. After degradation, the linear segments of polyDXL became cyclized molecules. The networks' structure, swelling behavior, and degradation were characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry, GC-MS analysis, and swelling data. This kind of material can be potentially used in biosystems, such as in intelligent drug-delivery systems. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1678–1682, 2002

Key words: pH-sensitive networks; degradation; poly(1,3-dioxolane)

INTRODUCTION

A new conception of a “telechelic bismacromonomer” was recently described as a polymer containing two polymerizable end groups.¹ Copolymerization of bismacromonomers with other monomers is expected to lead to polymer networks in which homopolymeric segments of one monomer are connected by macromonomer segments. Since polyacetal (polyDXL) has a low ceiling temperature, the thus-obtained networks contain segments which are expected to degrade to a monomer by treatment with a trace of an appropriate cationic initiator.² Until now, the poly(1,3-dioxolane) telechelic bismacromonomers have been

synthesized by different methods,^{3,4} but few polymer networks were prepared. Among the reported networks containing polyDXL segments are an elastic material by copolymerization with styrene and an amphiphilic polymer network by copolymerization with methyl methacrylate (MMA) prepared by Goethals' group.⁵

In this article, a novel pH-sensitive network was prepared by copolymerization of a polyDXL telechelic bismacromonomer with acrylic acid (AA). As we know, poly(acrylic acid) (PAA) is characterized as pH-sensitive.^{6,7} So, the networks containing its homopolymeric segments should give the polymer networks the same sensitivities. Also, due to the ease of degradation of polyDXL in acid, the networks can be decrosslinked. Accordingly, this kind of new material based on polyacetal segments will have some interesting physical properties and have wide applications in biosystems, such as in intelligent drug-delivery systems.

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EXPERIMENTAL

Reagents

1,3-Dioxolane (Acros Organics) was purified by distillation over CaH_2 and dried on sodium wire under reflux in the presence of a trace of benzophenone until a blue color was obtained. The monomer was distilled just before use (bp 74°C). Dichloromethane was distilled twice over CaH_2 . The solvent was distilled just before use. Triflic acid was purified by distillation. AA was distilled in a trace of benzoquinone. Dried pyridine was obtained by distillation in KOH.

Synthesis of $\alpha\omega$ -Dihydroxylated polyDXL (I)

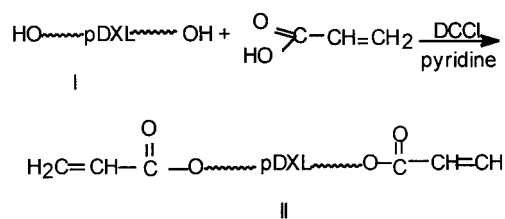
Fifteen microliters of $\text{CF}_3\text{SO}_3\text{H}$ in 10 mL of a CH_2Cl_2 solution was placed in a 50-mL flask provided with a stirrer and an inlet for dry nitrogen. Then, 0.2 mL ethylene glycol was added to the bottle. With stirring, 20 mL dioxolane was added dropwise to the system. The mixture was stirred for 3 h and thermostated at 50°C ; finally, an excess amount of *tert*-butylamine was added to stop the reaction. The reaction mixture was poured out into a beaker and precipitated in cold ether and washed several times with ether. Then, the precipitate was dried under a vacuum. **I**, 15.5 g (yield 80%) with an $M_n = 2500$, was obtained.

Synthesis of polyDXL Bismacromonomer.

Ten grams of OH-polyDXL-OH ($M_n = 2500$) and 10 mL of pyridine were placed in a flask provided with a stirrer and an inlet for dry nitrogen. One milliliter AA was introduced. Then, 2 g dicyclohexanecarbodiimide in a 5 mL CH_2Cl_2 solution was added dropwise. The mixture was thermostated at 25°C for 2 h. The mixture was washed with cold ether several times. The precipitate was dried under a vacuum. PolyDXL diacrylate (PDXLDA), 8.5 g (yield 85%), was obtained.

Polymer Networks Synthesis

Ten milliliters of toluene, 1 g PDXLDA, 5 mg of 2,2'-azobis(2-methylproprionitrile), and a certain amount of the comonomer were placed in a 20-mL test tube. The tube was sealed under a vacuum at 70°C for 16 h. A piece of gel was obtained. To remove unreacted monomers, the product was sequentially extracted with dichloromethane and ethanol. After being dried under a vacuum, the



DCCl: dicyclohexylcarbodiimide

Scheme 1

gel was cut into round thin slims and its swelling degree and its degradation in acid characterized.

Degradation in Acid Solution

The polymer network, 0.2 g, was placed in 10 mL of a 0.01 mol L^{-1} triflic acid solution in CH_2Cl_2 or other solvents. The degradation time was measured as the time necessary to dissolve the material completely.

RESULTS AND DISCUSSION

Synthesis of PolyDXL Bismacromonomer

Dihydroxylated polyDXL (HO-polyDXL-OH) (**I**) was prepared according to a method established by Franta et al.⁸ Also, the synthesis of the polyDXL bismacromonomer was based on acrylation of **I** with AA, as shown in Scheme 1.

This esterification reaction is carried out quantitatively without a side reaction. According to this reaction, polyDXL bismacromonomer **II**-polyDXL diacrylate (PDXLDA) was produced. The FTIR spectra of the original polyDXL and the resulting PDXLDA are shown in Figure 1. The difference appears at 1638 and 1720 cm^{-1} , which are attributed to the stretching of the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ of the ester structure, respectively. In polyDXL, no peaks appear, while in PDXLDA, both peaks appear. Evidently, PDXLDA was an ester product of polyDXL.

Synthesis and Characterization of pH-sensitive Poly(AA-*b*-DXL) Networks

The PDXLDA copolymer with different monomers can determine the properties of the networks. In this article, the comonomer AA was selected to prepare polyDXL-based networks with interesting physical properties. All the radical copolymerization was conducted in toluene at 70°C with

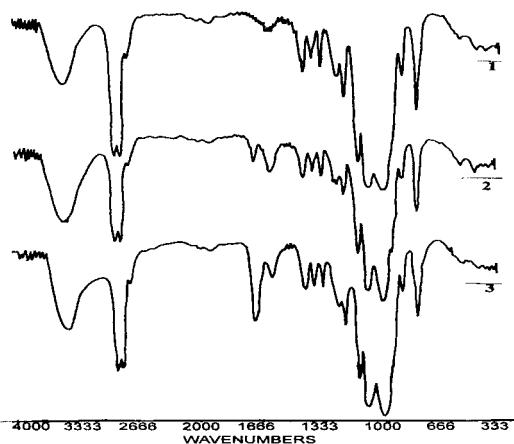


Figure 1 FTIR spectrum of macromonomers: (1) polyDXL; (2) PDXDA; (3) poly(AA-*b*-DXL); M_n (polyDXL) = 2500.

2,2'-azobis(2-methylpropionitrile) as the initiator. The end products were transparent networks [poly(AA-*b*-DXL)] with good elasticity. Figure 1 shows the IR spectrum of polymer networks [poly(AA-*b*-DXL)] in which the stretching of C=C was weakened and C=O was strengthened more than was PDXLDA. This shows that the radical copolymerization of PDXLDA with AA does occur.

As we know, PAA is well known as a pH-sensitive gel which is due to the —COOH groups. Similarly, the polymer networks with homopolymeric segments of AA should also be expected to have pH-sensitivity. Figure 2 testifies to this result. The swelling behavior of the poly(AA-*b*-DXL) networks is sensitive to the pH values of water. The swelling degree is calculated from

$$sd = (ws - wd)/wd \times 100\%$$

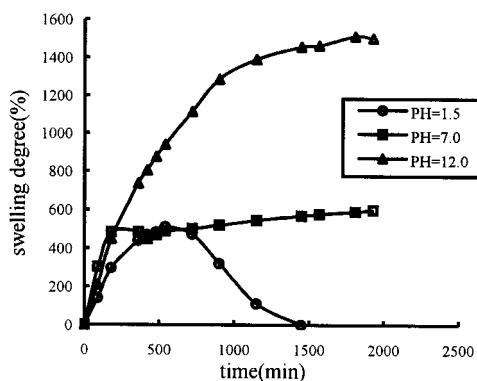


Figure 2 Swelling kinetics of the networks in water of different pH polymer networks: [polyDXL]/[AA] = 1 : 3 mol/mol; M_n (polyDXL) = 2500.

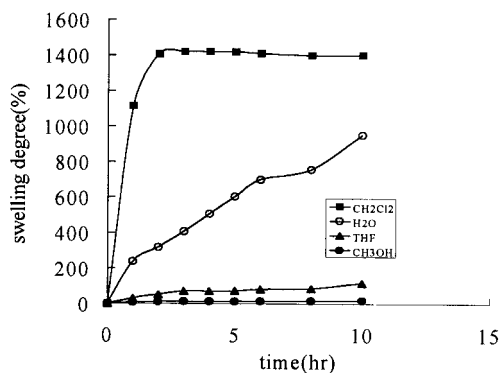


Figure 3 Swelling behavior of networks in different solvent networks: [polyDXL]/[AA] = 1 : 3 mol/mol; M_n (polyDXL) = 2500.

where ws is the swelling sample and wd is the dried gel sample. The swelling degree of the networks is influenced mainly by the ionization of —COOH functions in water. In pH 1.5, —COOH can hardly be ionized; thus, the formed strong hydrogen bonds among carbonyl groups prevent water to permeate into the networks. So, the networks swell slowly and have the lowest equilibrium swelling degree. As shown in the pH 1.5 curve, the networks began to degrade in 10 h, and after 24 h, the networks can be dissolved completely in water. However, in pH ≥ 7.0 , the networks can swell only until reaching the equilibrium swelling degree, but cannot be decrosslinked in water. With higher basicity, the networks can reach a higher equilibrium swelling degree.

The networks prepared can also swell in organic solvents. Figure 3 shows that in CH_2Cl_2 the networks swell fast and have the highest equilibrium swelling degree and then in H_2O , THF, and CH_3OH the swelling degree decreases that order. With increase of the PAA content in the networks, the swelling degree in organic solvents is also greatly influenced. Figures 4–6 support this result. In CH_2Cl_2 , the swelling degree decreases with increase of the AA content. It is contrary to the situation in CH_3OH , while in THF the swelling degree of the networks has a balanced value. With the [polyDXL]/[PAA] = 1:15, the networks reached the highest swelling degree. As a result, the swelling behavior of the networks is solvent-dependent and composition-dependent.

The property that the networks can swell in both water and organic solvents is interesting because they acted like amphiphilic networks in which this behavior can be explained by a microphase-separated bicontinuous structure.⁹ DSC

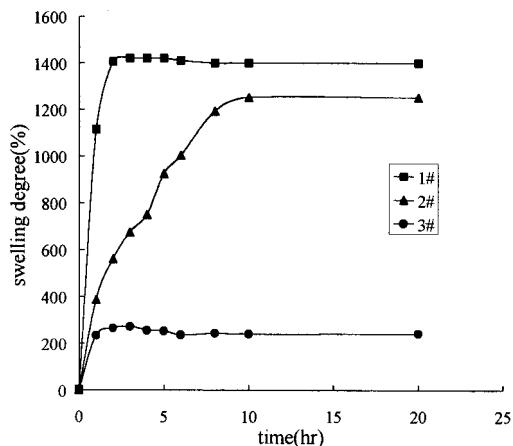


Figure 4 Swelling behavior of networks in CH_2Cl_2 : (1) $[\text{polyDXL}]/[\text{AA}] = 1 : 1.5$; (2) $[\text{polyDXL}]/[\text{AA}] = 1 : 15$; (3) $[\text{polyDXL}]/[\text{AA}] = 1 : 30$ mol/mol; M_n (polyDXL) = 2500.

analysis gives further support to the hypothesis of a microphase-separated structure of the prepared networks. Figure 7 shows a DSC analysis of polyDXL and polymer networks of poly(AA-*b*-DXL) under the same heating process. Both of them show an endotherm at 50°C which is due to the melting of the crystalline polyDXL, while in the latter another endotherm at 27°C appeared due to the copolymerization with PAA. Because the polyDXL segments act as crosslinking agents in the networks and the two chain segments of polyDXL and PAA possess different flexibility, the polymer networks show a microphase-separated interconnecting structure.

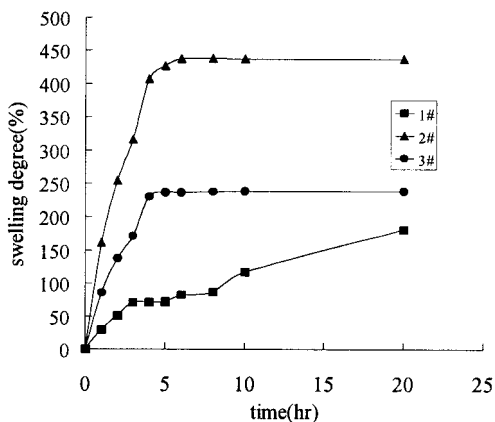


Figure 5 Swelling behavior of networks in THF: (1) $[\text{polyDXL}]/[\text{AA}] = 1 : 1.5$; (2) $[\text{polyDXL}]/[\text{AA}] = 1 : 15$; (3) $[\text{polyDXL}]/[\text{AA}] = 1 : 30$ mol/mol; M_n (polyDXL) = 2500.

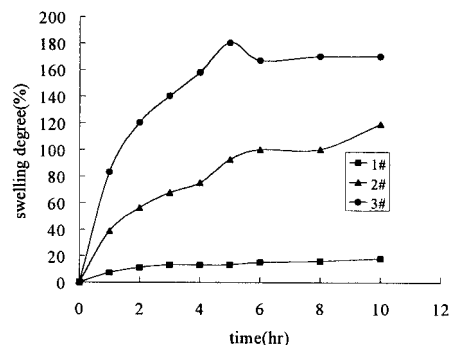


Figure 6 Swelling behavior of networks in CH_3OH : (1) $[\text{polyDXL}]/[\text{AA}] = 1 : 1.5$; (2) $[\text{polyDXL}]/[\text{AA}] = 1 : 15$; (3) $[\text{polyDXL}]/[\text{AA}] = 1 : 30$ mol/mol; M_n (polyDXL) = 2500.

Degradation of the Networks

All polymer networks prepared can degrade completely in an acid solution. Degradation of poly(AA-*b*-DXL) is shown in Figure 2. In pH 1.5 water, the networks can degrade completely in 24 h. From Table I it follows that the networks with different constituents can degrade within different times. With increase of the polyDXL content, the networks degrade fast, and with increase of the PAA content, the networks need more time to degrade. The properties of the solvents in which the networks can swell also had a great influence on the degradation. The networks AA-*b*-90 can degrade in CH_2Cl_2 in no more than 2 h under the same acidic condition. After 1-h degradation (incomplete) of these networks (with $[\text{CF}_3\text{SO}_3\text{H}] = 0.01$ mol L^{-1}) in CH_2Cl_2 , there was still some residue left in the bottle and most fragments were solved in CH_2Cl_2 . Both of them were

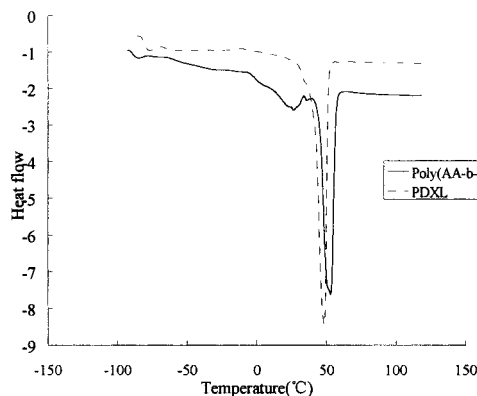


Figure 7 DSC analysis of poly(AA-*b*-DXL) networks and polyDXL: M_n (polyDXL) = 2500; $[\text{polyDXL}] : [\text{AA}] = 1 : 3$ mol/mol.

determined. Figure 8 shows FTIR spectra of the networks and the degraded residues. Only peaks of PAA were found in the latter; no peak was found at 1024–1120 cm^{-1} which belonged to C—O—C functions of polyDXL. This proved that the networks in which polyDXL acts as a polymeric crosslinking agent had been decrosslinked. By GC–MS analysis of the degraded solution in CH_2Cl_2 , 1,3-dioxolane, 1,3,5-trioxepane, and 1,3,6-trioxocane were found in the degraded solution. This also proved that degradation did occur.

CONCLUSIONS

The polymer networks containing polyDXL segments with pH-sensitivity or other special physical properties can be prepared by copolymerization of the polyDXL bismacromonomer with different monomers which determine the properties of the networks. The networks as a combination of these two segments possess two important physical properties: swelling and degradation. The swelling behavior of the polymer networks prepared in this article is solvent-dependent and composition-dependent. Degradation is also influenced by the solvents, acid concentration, etc. After degradation, the linear segments of polyDXL became cyclized molecules. Based on this study, more attention could be paid to this type of new material.

Table I Degradation of Networks with Different Constituents in pH 1.5 Water at 15°C

Networks	pH	Degradation Time
AA-b-95	1.5	150 hr
AA-b-90	—	180 hr
AA-b-65	—	300 hr
AA-b-50	—	~ 300 hr

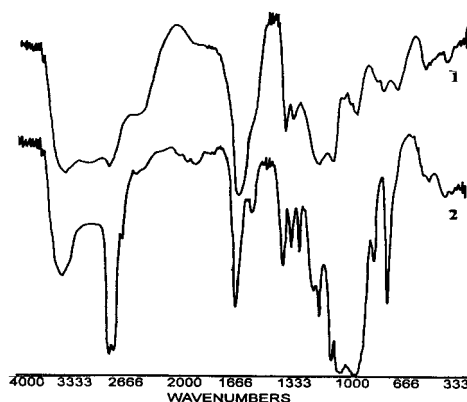


Figure 8 FTIR spectrum of polymer networks [poly(AA-*b*-DXL)] and degraded residues: (1) degraded residues; (2) polymer networks. M_n (polyDXL) = 2950; [pDXL]/[AA] = 1 : 3 mol/mol.

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